Synthesis, Crystal and Molecular Structure of Bis(tetraethylammonium) Bis(μ-ethylthio)-bis(μ-ethylthioxanthato)-bis[trithiocarbonatoiron(III)]

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Bis(tetraethylammonium) bis(μ-ethylthio)-bis(μ-ethylthioxanthato)-bis [trithiocarbonatoiron(III)], $[(C_2H_5)_4N]_2[Fe(SC_2H_5)(S_2CSC_2H_5)(CS_3)]_2$ *has been isolated as a decomposition product from a dilute acetonitrile solution of tetraethylammonium tris(ethylthioxanthato)iron(II)* $[(C_2H_5)_4N][Fe(S_2CSC_2H_5)_3]$*. The crystal and molecular structure of* $[(C_2H_5)_4N]_2[Fe(SC_2H_5)(S_2CSC_2H_5)(CS_3)]_2$ *was determined from three-dimensional X-ray data. The compound crystallizes in the monoclinic space group* $P2_1/n$ *with* $a = 10.442(3)$, $b = 9.809(3)$, $c = 21.728(6)$ Å, $\beta = 94.62(2)°$, $V = 2218.3$ Å^3 *and* $Z = 2$.

The structure was solved by the Patterson method. Least-squares refinements using 3656 unique reflections with $|F_o| > 3.92\sigma(F_o)$ *converged to* $R_1 = 0.044$ *and* $R_2 = 0.041$*. The iron atoms in the centrosymmetric complex* $[Fe(SC_2H_5)(S_2CSC_2H_5)(CS_3)]_2^{2-}$ *have a distorted octahedral coordination and are bridged by two ethylthio and two ethylthioxanthato ligands. Two trithiocarbonato ligands are bonded terminally to the iron atoms, resulting in four-membered chelate rings with two endocyclic C–S bonds (mean bond length 1.720 Å) and a shorter exocyclic one (1.666(3) Å). The geometry of the* $[Fe(SC_2H_5)(S_2CSC_2H_5)]_2^{2+}$ *moiety with a Fe–Fe distance of 2.614(1) Å indicates a direct metal–metal interaction.*

Introduction

Bidentate ligands of the type XCS_2^-, where X is SR (thioxanthates), OR (xanthates) or NR_2 (dithiocarbamates), do not form tetrahedral iron complexes because of their small S---S bite distances. However, a number of complexes has been described in which iron atoms are five- or six-coordinated by such ligands. $[Fe(S_2COC_2H_5)_3]$ and $[Fe(S_2CN(n\text{-}C_4H_9)_2)_3]$ are reported to have strongly distorted trigonal prismatic configurations [1, 2], while the coordination of the iron atom in the $[Fe(S_2CS\text{-}t\text{-}C_4H_9)_3]$ molecule is distorted octahedral [3]. The dimeric complex $[Fe_2(S_2CN(C_2H_5)_2)_4]$ formally consists of two $[Fe(S_2CN(C_2H_5)_2)_2]$-moieties connected by two common sulfur atoms, resulting in a Fe···Fe distance of 3.350 Å which lies beyond the range of metal–metal bonds [4]. The complex $[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2$ is also dimeric with a comparatively small iron–iron distance of 2.618(2) Å, which is 0.39 Å smaller than the bite distance of the sulfur atoms in the bridging ethylthioxanthato ligands. Furthermore, the Fe–S–Fe angles at the sulfur atoms of the μ-ethylthio ligands are small (72.35(7)°). These aspects of the iron–ligand geometry are interpreted as a consequence of the Fe–Fe bonding [5].

During our investigations of iron complexes with 1.1-dithio ligands we found that a dilute solution of $[(C_2H_5)_4N][Fe(S_2CSC_2H_5)_3]$ in acetonitrile decomposes to yield a small amount of crystalline $[(C_2H_5)_4N]_2[Fe(SC_2H_5)(S_2CSC_2H_5)(CS_3)]_2$. A structural comparison of the dianion in this compound and the closely related $[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2$ complex mentioned above is of particular interest. $[Fe(SC_2H_5)(S_2CSC_2H_5)(CS_3)]_2^{2-}$ is formally derived from $[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2$ by loss of two $C_2H_5^+$ groups at the non-bridging ethylthioxanthato ligands. The anion of the title compound is the first iron–sulfur complex with trithiocarbonato ligands, whose structure has been determined from single-crystal X-ray data. As far as we know only two other trithiocarbonato complexes of transition metals have been investigated by X-ray structural analysis [6, 7].

Experimental

Preparation of the Compound

Among the different possibilities of preparing ethylthioxanthate [8] we chose the interaction of carbon disulfide with ethylthiol in a concentrated aqueous solution of potassium hydroxide. Yellow crystals of potassium ethylthioxanthate were dried *in vacuo* and used for the following reaction which was carried out under nitrogen atmosphere.

$KS_2CSC_2H_5$ (7.1 g, 40 mmol) was dissolved in 30 ml of methanol and added to a stirred solution of $FeCl_2 \cdot 4H_2O$ (2.0 g, 10 mmol) in 25 ml of methanol. After stirring for 20 h at ambient

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temperature the reddish-brown mixture was filtered. When treated with 2.1 g (10 mmol) of $(C_2H_5)_4NBr$ the colour of the filtrate changed to dark green, and a black precipitate of $[(C_2H_5)_4N][Fe(S_2CSC_2H_5)_3]$ separated. A dilute solution of this product in acetonitrile was prepared and stored for several days at 10 °C. During this period the initial blue-green colour disappeared; besides amorphous brown products, black quadratic crystal plates of the title compound could be isolated in low yields. These crystals were suitable for X-ray structural analysis.

$[(C_2H_5)_4N][Fe(S_2CSC_2H_5)_3]$ can be recrystallized from concentrated solutions in acetonitrile to give large black crystals. The crystal and molecular structure of the analogous tetramethylammonium salt was determined by X-ray methods [9].

X-ray Data, Structure Solution and Refinement

A single crystal of the title compound was used for X-ray measurements. X-ray intensity data were collected on a Syntex $P2_1$ four-circle diffractometer equipped with a molybdenum tube, a graphite monochromator and a scintillation counter. During data collection the crystal was cooled by a cold stream of gaseous nitrogen. The unit cell parameters were obtained by least-squares refinement from diffractometer coordinates of 15 high-order reflections. They are given in Table I, together with relevant information concerning crystal data and experimental conditions. The intensity of a standard reflection (600) measured every 99 reflections did not show any significant changes during data collection. Systematic absences are characteristic for the space group $P2_1/n$. The data reduction was done by applying Lorentz and polarization corrections. An empirical absorption correction using intensity profiles of selected reflections (ψ-scan) was applied.

The structure was solved by the heavy-atom method. A three-dimensional Patterson synthesis revealed the positions of the iron and sulfur atoms of the FeS_6 coordination unit. The positions of the other non-hydrogen atoms were obtained from least-squares refinements, followed by subsequent difference Fourier syntheses. After refinement of the initial structural model with anisotropic thermal vibrations, a disorder of the bridging ligands became obvious. The population of the ethylthio group refined to approximately 0.67 and 0.33 respectively for two alternative orientations and was fixed at these values in the final refinements. In addition, for two sulfur atoms of the ethylthioxanthato group two slightly different positions could be resolved. The hydrogen atom positions of the cation and the ethylthioxanthato ligand were obtained by difference Fourier syntheses, but due to the disorder only two hydrogen atoms of the ethylthio group could be located. The atomic scattering factors for Fe, S, N, C (neutral spherical atoms) and H (spherical bonded atom) were taken from International Tables [10]. Full-matrix least-squares refinement with anisotropic temperature factors for most of the non-hydrogen atoms and isotropic temperature factors for the remaining atoms converged at $R_1 = 0.044$ and $R_2 = 0.041$. A final difference Fourier map revealed no peaks greater than 0.7 e/Å^3. All regions with residual electron densities greater than 0.4 e/Å^3 were found in the neighbourhood of the atoms which are affected by disorder. Atomic coordinates and thermal parameters of the final structural model, together with the occupancy factors of the disordered atoms, are given in Table II.

Results and Discussion

The structure of the title compound (*1*) consists of discrete $[Fe(SC_2H_5)(S_2CSC_2H_5)(CS_3)]_2^{2-}$ anions and tetraethylammonium cations. A thermal ellipsoid plot of the anion containing the atomic numbering scheme is given in Fig. 1. Figure 2 shows a stereoscopic view of the unit cell. Bond lengths and angles of the anion are summarized, together with selected intramolecular distances, in Table III. The following discussion, as well as the figures and Table III, refer to the predominantly occupied positions of the disordered ligands.

TABLE I. $[(C_2H_5)_4N]_2[Fe(SC_2H_5)(S_2CSC_2H_5)(CS_3)]_2$: Crystal Data and Experimental Conditions.

Molecular formula	$C_{28}H_{60}Fe_2N_2S_{14}$
Formula weight	985.4
Temperature	−130 °C
Crystal system	monoclinic
Space group	$P2_1/n$
a	10.442(3) Å
b	9.809(3) Å
c	21.728(6) Å
β	94.62(2)°
V	2218.3 Å^3
Z	2
Calculated density	1.475 g cm^{-3}
Absorption coefficient	13.2 cm^{-1}
Radiation	$MoK\bar{\alpha}$ ($\lambda = 0.71069$ Å)
Data collection range	$3° \leqslant 2\theta \leqslant 54°$
Scan speed	variable (between 4 and 30°/min depending on absolute intensity)
No. of independent data collected	4890
No. of observed data ($\lvert F_o \rvert > 3.92\sigma(F_o)$)	3656
No. of variables	327
$R_1 = \Sigma \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \Sigma \lvert F_o \rvert$	0.044
$R_2 = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2 / \Sigma w \lvert F_o\rvert^2]^{1/2}$	0.041

TABLE II. $[(C_2H_5)_4N]_2[Fe(SC_2H_5)(S_2CSC_2H_5)(CS_3)]_2$: Coordinates, Occupancy Factors of the Disordered Atoms and Coefficients of the Temperature Factors[a] [Å^2] with Standard Deviations.

Atom	Occupancy	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe		0.00197(5)	0.02384(5)	0.05924(2)	1.80(2)	1.60(2)	1.20(2)	0.06(2)	0.39(2)	−0.12(2)
S(1)		0.10459(8)	−0.03782(10)	0.15407(4)	1.70(4)	1.88(4)	1.46(3)	0.13(3)	0.34(3)	−0.06(3)
S(2)		−0.08848(9)	0.15462(10)	0.13439(4)	2.45(4)	2.11(4)	1.57(4)	0.58(3)	0.46(3)	−0.18(3)
S(3)		0.02519(10)	0.11218(10)	0.26576(4)	2.96(5)	2.11(4)	1.37(4)	−0.06(3)	0.59(3)	−0.20(3)
S(4)		−0.14433(10)	−0.14081(11)	0.07882(4)	2.78(5)	3.07(5)	1.40(4)	−1.15(4)	0.53(3)	−0.31(3)
S(5)	0.81(2)	−0.1358(6)	−0.2050(5)	−0.05661(8)	3.12(16)	2.42(11)	1.33(6)	−0.90(12)	0.61(6)	−0.25(5)
S(5a)	0.18(2)	−0.1773(14)	−0.1694(14)	−0.0593(33)	1.55(18)[b]					
S(6)	0.88(1)	−0.30123(34)	−0.36055(34)	0.01323(6)	5.09(15)	4.39(13)	1.67(5)	−3.15(12)	0.65(5)	−0.31(5)
S(6a)	0.10(1)	−0.3530(17)	−0.3078(19)	0.0133(6)	2.40(32)					
S(7)	0.67	0.14928(15)	−0.09400(17)	0.01260(7)	1.38(6)	1.77(7)	1.56(5)	0.02(5)	0.53(5)	−0.04(5)
S(7a)	0.33	0.09440(32)	−0.14960(35)	0.01419(13)	1.67(13)	2.33(14)	1.45(11)	0.10(11)	0.39(9)	−0.10(10)
C(1)		0.01364(33)	0.07894(37)	0.19033(16)	1.58(15)	1.55(15)	1.80(14)	−0.57(12)	0.66(11)	−0.18(12)
C(2)		−0.19342(40)	−0.22402(43)	0.01377(17)	3.42(20)	3.09(20)	1.74(16)	−1.62(16)	0.59(14)	0.02(14)
C(3)		−0.3380(5)	−0.3843(5)	0.09220(19)	3.88(24)	3.59(24)	1.92(17)	−1.38(19)	0.81(16)	−0.16(16)
C(4)		−0.3924(6)	−0.5261(6)	0.09640(24)	5.96(32)	3.50(24)	2.77(21)	−1.50(25)	1.67(21)	−0.01(19)
C(5)	0.67	0.1462(5)	−0.2779(6)	0.02876(25)	2.01(10)					
C(5a)	0.33	0.2689(13)	−0.1349(14)	0.0171(6)	3.21(25)					
C(6)	0.67	0.2707(6)	−0.3139(7)	0.06902(30)	3.05(12)					
C(6a)	0.33	0.3283(12)	−0.2535(14)	0.0590(6)	2.75(23)					
C(7)		−0.15134(35)	−0.44096(42)	0.26262(20)	1.29(15)	2.41(19)	2.75(18)	0.42(13)	0.44(13)	−0.11(15)
C(8)		−0.20551(47)	−0.5841(49)	0.26084(24)	1.87(19)	2.65(20)	4.03(23)	−0.30(16)	0.63(17)	−0.62(18)
C(9)		0.02410(37)	−0.28007(40)	0.27825(19)	2.13(17)	1.49(16)	2.81(18)	0.38(13)	0.61(14)	0.16(14)
C(10)		0.16328(43)	−0.24465(47)	0.29343(24)	2.58(19)	1.89(19)	3.74(22)	−0.27(15)	−0.03(17)	0.45(16)
C(11)		0.03140(42)	−0.49577(44)	0.34054(19)	2.38(19)	2.21(20)	2.84(18)	0.13(15)	0.41(14)	0.83(14)
C(12)		−0.0281(6)	−0.4334(6)	0.39507(23)	3.69(27)	4.71(31)	2.74(21)	−0.04(23)	0.73(19)	−0.54(19)
C(13)		0.06572(41)	−0.50764(43)	0.23121(20)	2.09(18)	1.97(19)	3.42(19)	0.48(14)	1.20(14)	−0.22(14)
C(14)		0.0389(7)	−0.4639(6)	0.16553(23)	5.59(33)	2.99(25)	3.28(22)	0.35(24)	2.24(22)	−0.43(20)
N		−0.00792(28)	−0.43096(31)	0.27845(14)	1.61(13)	1.51(13)	2.46(14)	0.12(10)	0.64(10)	−0.01(10)

[a] The anisotropic temperature factor is defined as $\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. [b] The temperature factors of the isotropic atoms are given as B_{11}.

TABLE III. $[(C_2H_5)_4N]_2[Fe(SC_2H_5)(S_2CSC_2H_5)(CS_3)]_2$: Intramolecular Distances and Angles of the Anion[a].

Distances [Å]:		Angles [°]:	
Fe–Fe'	2.614(1)	Fe'–Fe–S(1)	142.76(3)
Fe–S(1)	2.325(1)	Fe'–Fe–S(2)	144.28(3)
Fe–S(2)	2.335(1)	Fe'–Fe–S(4)	95.68(3)
Fe–S(4)	2.286(1)	Fe'–Fe–S(5')	94.39(2)
Fe–S(5)	2.264(5)	Fe'–Fe–S(7)	54.33(4)
Fe–S(7)	2.231(2)	Fe'–Fe–S(7')	54.10(4)
Fe–S(7')	2.238(2)	S(1)–Fe–S(2)	72.94(4)
S(1)–C(1)	1.719(4)	S(1)–Fe–S(4)	85.33(4)
S(2)–C(1)	1.720(4)	S(1)–Fe–S(5')	89.15(3)
S(3)–C(1)	1.666(3)	S(1)–Fe–S(7)	88.99(5)
S(4)–C(2)	1.676(4)	S(1)–Fe–S(7')	161.33(5)
S(5)–C(2)	1.698(4)	S(2)–Fe–S(4)	86.80(4)
S(6)–C(2)	1.749(5)	S(2)–Fe–S(5')	82.62(3)
S(6)–C(3)	1.803(4)	S(2)–Fe–S(7)	159.15(5)
S(7)–C(5)	1.838(6)	S(2)–Fe–S(7')	90.94(5)
C(3)–C(4)	1.509(8)	S(4)–Fe–S(5')	169.13(4)
C(5)–C(6)	1.549(9)	S(4)–Fe–S(7)	102.34(5)
S(1)···S(2)	2.770(1)	S(4)–Fe–S(7')	84.40(5)
S(1)···S(3)	3.011(1)	S(5')–Fe–S(7)	86.89(4)
S(2)···S(3)	3.031(1)	S(5')–Fe–S(7')	98.25(4)
S(4)···S(5)	3.017(1)	S(7)–Fe–S(7')	108.42(6)
S(4)···S(6)	2.998(3)		
S(5)···S(6)	2.835(3)		
		Fe–S(1)–C(1)	90.04(12)
		Fe–S(2)–C(1)	89.68(12)
		Fe–S(4)–C(2)	110.53(15)
		Fe–S(5')–C(2')	111.91(14)
		Fe–S(7)–Fe'	71.58(5)
		Fe–S(7)–C(5)	113.5(2)
		Fe'–S(7)–C(5)	114.4(2)
		C(2)–S(6)–C(3)	106.2(3)
		S(1)–C(1)–S(2)	107.3(2)
		S(1)–C(1)–S(3)	125.6(2)
		S(2)–C(1)–S(3)	127.1(2)
		S(4)–C(2)–S(5)	126.8(3)
		S(4)–C(2)–S(6)	122.1(3)
		S(5)–C(2)–S(6)	110.6(2)
		S(6)–C(3)–C(4)	106.7(4)
		S(7)–C(5)–C(6)	107.8(4)

[a] The primed atoms are related to the unprimed ones by the symmetry transformation –x, –y, –z.

The binuclear anions are located on crystallographic inversion centers which imply the exact planarity of their central Fe_2S_2 cores. The iron atoms are symmetrically bridged by two ethylthio and two ethylthioxanthato ligands, and are additionally bonded to bidentate trithiocarbonato ligands. The $[Fe(SC_2H_5)(S_2CSC_2H_5)(CS_3)]_2^{2-}$ anion derives from the binuclear neutral $[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2$ complex [5] by substitution of the terminal thioxanthate groups with trithiocarbonato ligands. Thus each iron atom is surrounded by a distorted octahedron of six sulfur atoms. The Fe–S distances vary from 2.231(2) Å (Fe–S(7)) to 2.335(1) Å (Fe–S(2)), whereas the S–Fe–S angles are distributed between 72.94(4)° (in the four-membered chelate ring) and 108.42(6)° (in the central Fe_2S_2 rhomb).

The short Fe–Fe distance of 2.614(1) Å indicates metal–metal bonding. This is supported by two aspects of the geometry of the bridging ligands. Firstly the S···S bite distance (3.017(1) Å) of the ethylthioxanthato ligand is 0.400 Å larger than the separation of the iron atoms. Secondly the Fe–S–Fe angle at the ethylthio S atom has an average value of 72.06°. On the other hand the corresponding Co–S–Co angle (95.34(3)°) in the $[Co(SC_2H_5)(S_2CSC_2H_5)_2]_2$ dimer [11] is considerably larger. Accordingly the long Co···Co separation (3.321(2) Å) excludes direct metal–metal interaction.

The ethylthio ligand in crystals of (*1*) exist in two alternative orientations which are populated in a ratio of about 2:1. An additional disorder was found with respect to the ethylthioxanthato ligand, which can best be fitted by a superposition of two alternative sites of the sulfur atoms S(5) and S(6) having occupancy ratios of 0.8:0.2 and 0.9:0.1 respectively. Further split atom positions of the thioxanthato ligand could not be resolved, probably due to an overlap of the electron clouds. However, strongly anisotropic thermal vibrations of the remaining atoms of the thioxanthato ligand indicate further influence of the disorder.

Though the superposition of two partially resolved sites of the ethylthioxanthato ligand does not allow the evaluation of the exact geometry, the CS_3 moiety shows three significantly different S–C–S angles. The largest one ((S(4)–C(2)–S(5): 126.8(3)°) is found in the five-membered ring formed by the ligand and the two iron atoms. The other two S–C–S angles are 122.1(3) and 110.6(2)°, the larger one being S(4)–C(2)–S(6). This difference might be due

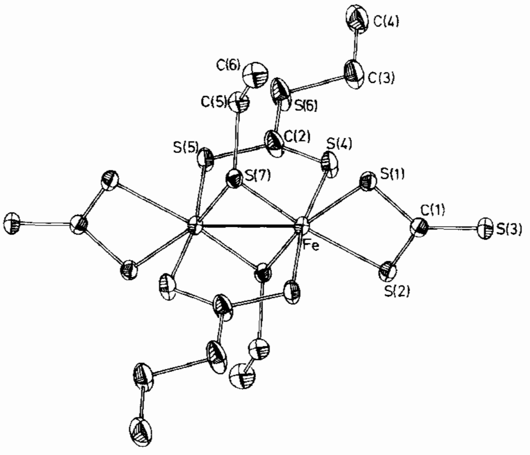


Fig. 1. $[(C_2H_5)_4N]_2[Fe(SC_2H_5)(S_2CSC_2H_5)(CS_3)]_2$: Thermal ellipsoid plot (50% probability) of the anion with atomic designations.

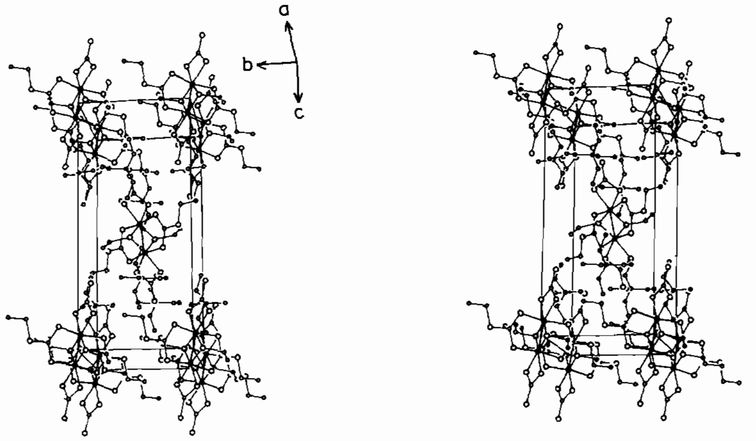
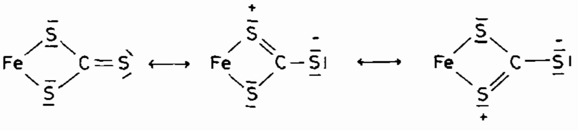


Fig. 2. $[(C_2H_5)_4N]_2[Fe(SC_2H_5)(S_2CSC_2H_5)(CS_3)]_2$: Stereoscopic view of the unit cell.

to a steric effect of the alkyl group. A similar effect has been described for $[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2$ [5]. As expected, the mean C–S bond length of 1.687 Å involving sulfur coordinated to iron lies between the values of 1.78 Å and 1.61 Å accepted for a C(sp^2)–S single and double bond respectively [12]. The exocyclic C–S bond has a length of 1.749(5) Å, which is shorter than a C(sp^2)–S single bond, indicating partial p_π–p_π bonding. The shortening of the exocyclic C–S bond is more pronounced in metal complexes containing thioxanthato ligands involved in four-membered chelate rings. In several of these complexes the bond referred to has a length of approximately 1.71 Å [3, 5, 11, 13]. The $[Fe(SC_2H_5)(S_2CSC_2H_5)]_2^{2+}$ moiety in the present compound and the corresponding part of the $[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2$ dimer [5] show extensive structural analogies.

The completely ordered planar trithiocarbonate groups (sum of the S–C–S angles: 360.0°) and the iron atoms form four-membered chelate rings with S–Fe–S angles of 72.94(4)°, resulting in a severe distortion of the octahedral iron coordination. In addition the angle at the carbon atom in the chelate ring is small with respect to the ideal value of an sp^2-hybridized atom. This can be considered a consequence of the ring strain, which also seems to give rise to a weakening of the Fe–S bonds (mean value: 2.330 Å). The average angle at the sulfur atoms of the chelate ring is 89.86°. In contrast to the corresponding angles in the ethylthioxanthato ligand the two exocyclic angles at C(1) are nearly equal (125.6(2) and 127.1(2)°). The two C–S bond lengths in the chelate ring (mean value: 1.720 Å) are similar to the C–SH bond lengths found in the two modifications of trithiocarbonic acid (mean value: 1.731 Å) [14, 15], but they are *ca.* 0.06 Å smaller than the value expected for a single bond (see above). This indicates a substantial contribution of the limiting structures II and III (besides I) to the ground state:



I II III

The assumption of a p_π–p_π delocalisation in the CS_3 skeleton of the trithiocarbonato ligand is supported by the length of the exocyclic C–S bond. The observed value (1.666(3) Å) is *ca.* 0.06 Å larger than the value expected for a double bond [12], and is also larger than the mean C–S bond length (1.647 Å) in trithiocarbonic acid [14, 15]. The average C–S bond length in the planar and regular CS_3^{2-} anion of $[(CH_3)_4N]_2CS_3 \cdot 4H_2O$ (d(C–S): 1.69 Å) is only slightly longer [16]. In the complex $[Ni(CS_3)_2]^{2-}$ the trithiocarbonato ligands also form four-membered chelate rings but the endocyclic C–S bond lengths (mean value: 1.70 Å) do not differ very much from the exocyclic one (1.68(2) Å) [6]. A rhenium complex has been reported which contains a CS_3 group bonded to three metal atoms [7]. The corresponding three C–S bond lengths are different: the shortest and largest ones (1.63(1) Å and 1.78(1) Å respectively) are close to the values expected for double and single bonds, whereas the third one (1.71(1) Å) can be compared with the mean C–S bond length (1.720 Å) observed in the four-membered chelate ring of (*1*).

The tetraethylammonium cations exhibit no unexpected structural properties. Distances and angles of the cation are given in Table IV.

The question concerning the mechanism of the conversion of $[Fe(S_2CSC_2H_5)_3]^-$ to $[Fe(SC_2H_5)(S_2CSC_2H_5)(CS_3)]_2^{2-}$ has still to be answered. The formation of the ethylthio group is probably

TABLE IV. $[(C_2H_5)_4N]_2[Fe(SC_2H_5)(S_2CSC_2H_5)(CS_3)]_2$: Intramolecular Distances and Angles of the Cation.

Distances [Å]:		Angles [°]:	
N–C(7)	1.512(5)	C(7)–N–C(9)	106.1(3)
N–C(9)	1.518(5)	C(7)–N–C(11)	111.5(3)
N–C(11)	1.518(5)	C(7)–N–C(13)	111.0(3)
N–C(13)	1.529(5)	C(9)–N–C(11)	111.5(3)
		C(9)–N–C(13)	110.8(3)
		C(11)–N–C(13)	106.0(3)
C(7)–C(8)	1.512(6)	N–C(7)–C(8)	115.3(3)
C(9)–C(10)	1.505(6)	N–C(9)–C(10)	115.7(3)
C(11)–C(12)	1.510(7)	N–C(11)–C(12)	115.4(4)
C(13)–C(14)	1.495(7)	N–C(13)–C(14)	115.7(4)

due to elimination of CS_2. This reaction is known to be typical of some metal thioxanthate complexes [17, 18]. The trithiocarbonato ligand is possibly formed by olefin elimination. Analogous reactions leading to dithiocarbonate complexes from metal xanthates have been described [19, 20]. The reaction system is still under study.

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